LBL-25838
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

Materials & Chemical Sciences Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JAN 25 1989

LIBRARY AND
DOCUMENTS SECTION

Submitted to Physical Review B

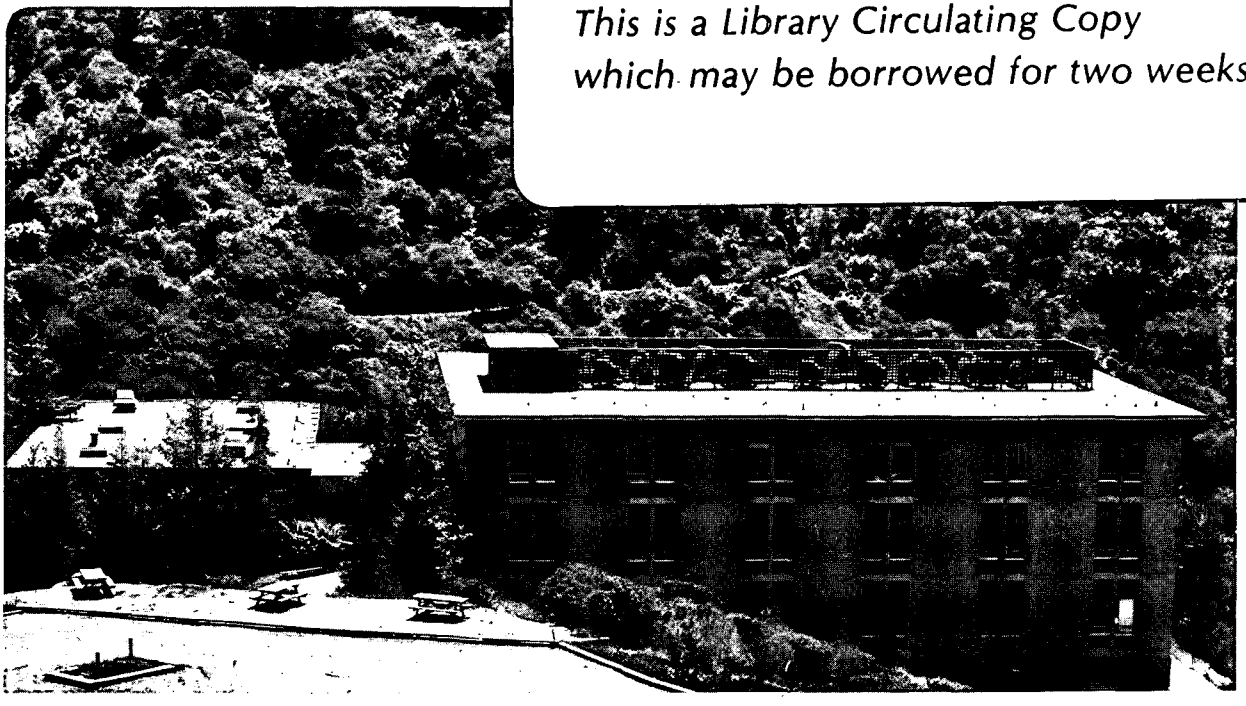
Reply to the Comment on "Geometry of (2x2)S/Cu(001) Determined with Use of Angle-Resolved Photoemission Extended Fine Structure"

D.A. Shirley, L.J. Terminello, and C.C. Bahr

August 1988

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.



LBL-25838

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-25838

Reply to the Comment on "Geometry of (2x2)S/Cu(001) Determined with Use of Angle-Resolved Photoemission Extended Fine Structure"

D.A. Shirley, L.J. Terminello, and C.C. Bahr*

Department of Chemistry, University of California
and
Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory
1 Cyclotron Road, Berkeley, California 94720

Zeng, et al.[1] have called attention to discrepancies averaging about 0.12Å in a set of eight structural parameters for the (2x2)S/Cu(001) surface structure, as derived from LEED versus ARPEFS data. This is a valuable observation, and the discrepancy must be resolved if we are to derive reliable surface structures of high accuracy. To this end we shall make several observations below. First, however, it is instructive to note that the accuracy and reliability of derived surface structures are improving over time, perhaps in no small measure because of our growing ability to bring two or more intrinsically accurate methods such as LEED and ARPEFS to bear on the same system. To add further perspective regarding these discrepancies, we note first that, in the recent past, LEED structures were often quoted with error limits of ±0.1Å in the structural parameters: it is encouraging that disagreement at this level is now (correctly) regarded as serious. Second, the sites of the adsorbed sulfur atoms are not in question: they adsorb in fourfold hollow sites. Third, some otherwise very valuable surface structural techniques would contribute little to resolving these subtle discrepancies. For example, surface extended x-ray absorption fine structure (SEXAFS) could confirm the Cu-S nearest-neighbor distance of 2.26(1)Å, and SEXAFS or scanning tunneling microscopy (STM) could confirm the hollow site, but these two results are not in doubt. Of special interest in this case is a test of the surprising LEED finding that adsorbate sulfur "spreads" the copper atoms in the Cu_5S moiety away from their normal lattice positions. This effect is probably too small to

be detected by SEXAFS or STM, and it should be confirmed if we are to understand the chemistry of this surface.

We cannot offer a unique explanation for this discrepancy, but we can narrow down the possibilities through a few observations. First, we computed an ARPEFS $\chi(k)$ curve for each of the three experimental directions from the LEED-derived parameters of Zeng, et al.[1] By visual inspection, each LEED-derived $\chi(k)$ curve gave a poorer fit to the ARPEFS data[2] than did either the published "best fit" curve or an ARPEFS curve based on the published[2] final structure. Thus the LEED structure doesn't "pass the ARPEFS test". We believe these comparisons do not warrant an R-factor analysis, but subjectively the fitted LEED I(E) curves appear to discriminate more strongly against the ARPEFS-derived structure (Fig. 2 for Zeng et al.[1]) than vice-versa.

Provided that the LEED and ARPEFS studies were really done on the same surface structure, which appears well-documented, we believe that the discrepancy is attributable to the interpretation of the data, rather than to the data per se. Expressed differently, we believe that either the LEED or the ARPEFS data are intrinsically of sufficiently high quality and sensitivity to yield accurate structural parameters through a sufficiently rigorous and accurate interpretation. Ideally both data sets should be interpreted together, using identical or equally rigorous theoretical approximations. Unfortunately we have not been able to make such a comparison as yet, for several reasons. Among these is the LEED practice of using a complex inner potential and taking the real part of this potential as an adjustable parameter. Zeng et al. refined their potential from -5.1 eV to an unspecified final value during the fitting process, while holding the imaginary part of the potential at -5.0 eV. In contrast, Bahr, et al. used a fixed real inner potential . Although the LEED analysis appears to fit the data better, we have difficulty evaluating the effect of taking a real physical parameter--the crystal potential--as complex, and treating the real part as an additional adjustable parameter to improve the fit. In particular, we are concerned about the possible coupling of derived "best-fit" values of structural and nonstructural parameters in

the LEED analysis. Perhaps we should not expect the structural parameters derived from the two analyses to agree exactly when the nonstructural parameters are so different. We note, by contrast, that for c(2x2)S/Ni(011), where this problem was not present, ion-scattering[3] and ARPEFS[4] studies yielded structural parameters in excellent agreement. In addition to the difficulty of separating structural from non-structural parameters in the fit of theory to data, both ARPEFS and LEED results assume a specific reconstruction model of the top Cu layer (puckering) and the second Cu layer (corrugation). The future refinement of both techniques may show that other hitherto untried models of surface reconstruction will prove satisfactory to LEED and ARPEFS measurements.

We concur that the (2x2)S/Cu(001) system may well provide a good case for comparing surface structural methods. More work is clearly needed.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. It was performed at the Stanford Synchrotron Radiation Laboratory, which is supported by the Department of Energy's Office of Basic Energy Sciences.

*Present address: AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974.

References

1. H.A. Zeng, R.A. McFarlane, and K.A.R. Mitchell, preceding Comment.
2. C.C. Bahr, J.J. Barton, Z. Hussain, S.W. Robey, J.G. Tobin, and D.A. Shirley, Phys. Rev. B35. 3773 (1987).
3. J.F. van der Veen, R.M. Tromp, R.G. Smeek, and F.W. Saris, Surf. Sci. 82, 468 (1979).

4. S.W. Robey, J.J. Barton, C.C. Bahr, G. Liu, and D.A. Shirley, Phys. Rev. B35, 1108 (1987).

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720